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Corrosion Behavior of $\text{Ni}_3(\text{Si,Ti})$ in Hydrochloric Acid Solution

Gadang Priyotomo^{#1}, Yasuyuki Kaneno^{*2}

[#]Research Center for Metallurgy, Indonesian Institute of Sciences

Kawasan PUSPIPTK Gd.474, Setu, Tangerang Selatan, Banten, Indonesia

¹gadangp@gmail.com

^{*}Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University

1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

²kaneno@mtr.osakafu-u.ac.jp

Abstract - The corrosion behaviour of the intermetallic compounds $\text{Ni}_3(\text{Si,Ti})$ (L_{12} : single phase), has been investigated using an immersion test, electrochemical method, scanning electron microscope in $0.5 \text{ kmol/m}^3 \text{ HCl}$ at 303 K . In addition, the corrosion behaviour of austenitic stainless steel type 304 and C276 was studied under the same experimental conditions as references. It was found that the intergranular attack was observed for $\text{Ni}_3(\text{Si,Ti})$ in the immersion test. From the immersion test and polarization curves, $\text{Ni}_3(\text{Si,Ti})$ had the moderate corrosion resistance, while the corrosion resistances of C 276 and type 304 were the highest and the lowest. $\text{Ni}_3(\text{Si,Ti})$ and type 304 were difficult to form a stable passive film, but not for C276. A further experiment must be conducted to clarify the stability of film for $\text{Ni}_3(\text{Si,Ti})$ in detail.

Keywords — Intermetallic Compound; Immersion Test; Polarization Curve; Passive film; Intergranular Attack

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I. INTRODUCTION

Takasugi and co-workers have reported that $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound with L_{12} structure has unique strength and ductility properties; that are , (1) an increase in flow strength with increasing temperature and (2) high ductility over a wide range of test temperatures (Takasugi et al.,1990 ; Takasugi et al.,1991). In particular, its strength level is extremely high as compared with that of other L_{12} ordered intermetallic compounds which has been developed as advanced materials (Kaneno et al., 2008), and the $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound is superior for conventional alloys such as steels, nickel base alloys, and stainless steel as low- and high- temperature structural materials. The $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound shows an excellent oxidation resistance in air, at ambient and elevated temperatures (Kaneno et al., 2007).

However, the $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound is susceptible to environmental embrittlement (specially hydrogen embrittlement) at ambient temperature in moist

environments (Takasugi et al., 1993a,b), where hydrogen embrittlement takes place with permeation of atomic hydrogen formed through corrosion reaction into the compound. The addition of small amount of boron to $\text{Ni}_3(\text{Si,Ti})$ is effective in suppressing environmental embrittlement (Takasugi et al., 1995). However, Priyotomo and co-workers have found that the boron segregation at grain boundaries become the preferential sites for corrosive dissolution and let to the intergranular attack for a homogenized $\text{Ni}_3(\text{Si,Ti})$ (Priyotomo et al.,2011; Priyotomo et al.,2012). Furthermore, Kaneno and co-workers already investigated the mechanical properties of $\text{Ni}_3(\text{Si,Ti})$ compounds after thermomechanical process had done(Kaneno et al.,2008; Kaneno et al.,2007). With regard to this compound, there is little study on the corrosion behavior in aqueous solution at ambient temperature, although the corrosion behavior of Ni_3Al , NiAlFe and Fe_3Al compounds was qualitatively investigated in acidic solutions (Dequette et al.,1994 ; Songbo et al.,2002 ; Colin et al.,2007). Therefore, the objective of this work is to

elucidate the corrosion behavior of $\text{Ni}_3(\text{Si,Ti})$ after thermomechanical process in HCl solution.

II. EXPERIMENTAL

A. The specimens

Ni-11 at.% Si-9.5 at.% Ti compound with the addition of 50 wt. ppm of boron, which was known to form an ordered L_{12} single phase of $\text{Ni}_3(\text{Si,Ti})$, was prepared by using an arc melting method under an argon gas atmosphere. It was homogenized at 1323K for 48 h under argon atmosphere and then cooled in vacuum furnace with cooling rate of 283 K/ min. Homogenized ingot was conducted a warm rolling at 573 K in air until obtaining the desired thickness and then a cold rolling until 1.2 mm of thickness in 75 % reduction. After obtaining cold-rolled thin sheet, this sheet was finally annealed from 873K to 1273K for 1 h. Type 304 of austenitic stainless steel as a reference was solution annealed at 1323 K for 1 h and then water quenched. Type of C-276 alloy also was as the reference for the experiments. The chemical and nominal compositions of steels as materials are given in Table 1.

Table 1: Composition and nominal of the materials investigated

Elements	$\text{Ni}_3(\text{Si,Ti})$	Type 304	C-276
At%			
C	-	0.027	0.52
Si	11.0	0.68	0.11
Mn	-	0.947	1.14
P	-	0.047	0.0081
S	-	0.006	0.058
Ni	-	7.6	57.95
Cr	-	19.3	19.21
Mo	-	-	10.41
V	-	-	0.37
Fe	-	71.4	6.15
Ti	9.5	-	-
W	-	-	4.5
Co	-	-	2.65
Part per million (ppm)			
B	50	-	-

B. Pretreatment of the specimens and test solutions

The homogenized specimens were cut into 1.2 mm x 9 mm x 15 mm. Then they were polished to 1.0 micrometer alumina paste, degreased by using acetone in an ultrasonic cleaner and washed with distilled water. The test solution, 0.5 kmol/m³ HCl solution, was made by using reagent grade chemicals and distilled water. For microstructure observation galvanostatic etching of the mechanically polished specimens was conducted in a solution that consist of 15 ml of 17.8 kmol/m³ H₂SO₄ and 85 ml of methanol at a current density of 0.446 A/cm² for 30 sec at 243K.

C. Corrosion tests

1) *Immersion test* : The immersion test of the mechanically polished specimen was conducted to get a weight loss (ΔW), the difference in weights of the specimens before and after the immersion test, at various immersion times up to a maximum time of 96 hours in HCl solution at 303 K under an open circuit condition. After

the experiments, the morphology of the specimen surfaces was investigated by using scanning electron microscope (SEM).

2) *Electrochemical test*: The potential method was used to measure polarization curves of the specimens in HCl solution that contacted with air at 303 K. The reference and counter electrodes used were Ag/AgCl saturated with KCl and a platinum sheet, respectively. Polarization measurements were conducted in a potential range from -800 mV to 1000 mV vs. Ag/AgCl where the potential was increased (anodic) or decreased (cathodic) from a corrosion potential with a potential interval of 100 mV (partly 50 mV) and was held for 10 minutes at each potential.

III. RESULTS AND DISCUSSION

A. Microstructure

$\text{Ni}_3(\text{Si,Ti})$ intermetallic compound is composed of single phase with L_{12} structure. The microstructure of the compound is shown in Fig.1. The microstructure of $\text{Ni}_3(\text{Si,Ti})$ with L_{12} that were observed, had equiaxial and boundaries grains. The similar microstructure was found for $\text{Ni}_3(\text{Si,Ti})$ as reported in the previous paper (Priyotomo et al.,2011). Kaneno and co-workers also have already described the microstructures of the intermetallic compound in detail (Kaneno et al., 2005).

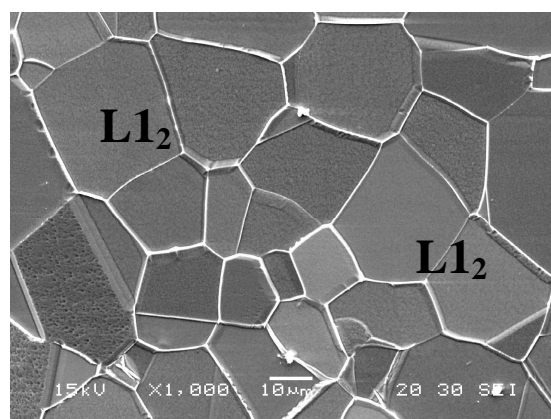


Fig.1 Microstructure of $\text{Ni}_3(\text{Si,Ti})$ before experiments

B. Weight loss, polarization test and surface morphology

Fig. 2 shows the change in weight loss with immersion time for $\text{Ni}_3(\text{Si,Ti})$, type 304 and C 276 in 0.5 kmol/m³ HCl solution at 303 K. The weight losses for these materials tended to increase with immersion time. The highest and lowest weight losses were type 304 and C 276. The corrosion resistance was found to be in order of C 276 > $\text{Ni}_3(\text{Si,Ti})$ > type 304.

Fig. 3 shows anodic and cathodic polarization curves of $\text{Ni}_3(\text{Si,Ti})$, type 304 and C 276 in 0.5 kmol/m³ HCl solution at 303 K. The anodic polarization curve of type 304 showed an active region with a peak of current density, a quasi-passive region with a relatively high anodic current density in a very narrow potential range, and a region showing an increase in anodic current density with potential. The anodic polarization curve of $\text{Ni}_3(\text{Si,Ti})$ had the same the active and quasi-passive region as type 304.

In the other hand, the anodic polarization curve of C 276 showed an active region with a very low peak current density and a wide passive region up to the oxygen evolution potential. The anodic current densities of $\text{Ni}_3(\text{Si,Ti})$ and type 304 in the quasi – passive region were in the range of 10^{-3} to 10^{-4} A/ cm^2 approximately, whereas that of C 276 in passive region was 10^{-6} A/ cm^2 . The corrosion current density estimated at the open circuit potential was found to be order of C 276 < $\text{Ni}_3(\text{Si,Ti})$ < type 304.

From the results obtained in Fig. 2 and Fig. 3, the following things summarized.

1. The corrosion resistance of type 304 was the lowest in HCl.
2. C 276 had the higher corrosion resistance than $\text{Ni}_3(\text{Si,Ti})$ and type 304 in HCl solution.
3. The results of the immersion test on all materials had a good correspondence with those of the polarization test.

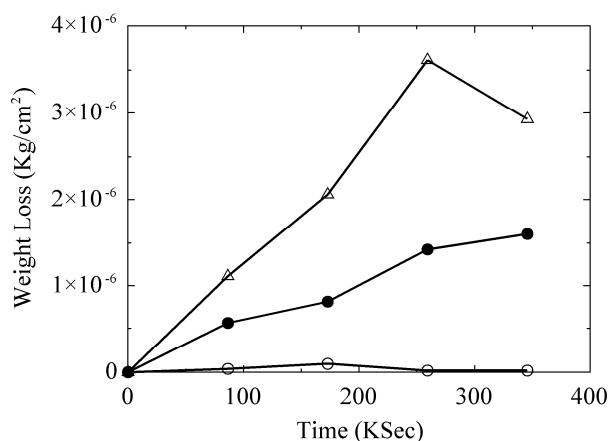


Fig. 2. The weight losses of ● $\text{Ni}_3(\text{Si,Ti})$, △ type 304 and ○ C 276 as a function of immersion time in 0.5 kmol/ m^3 HCl solution at 303 K.

Fig.4 shows the surface morphology of $\text{Ni}_3(\text{Si,Ti})$ after the immersion time of 96 hours in 0.5 kmol/ m^3 HCl solution. It was found that the surface morphology of $\text{Ni}_3(\text{Si,Ti})$ showed intergranular attack and uniform attack as well as that on as-homogenized $\text{Ni}_3(\text{Si,Ti})$ (Priyotomo et al.,2011; Priyotomo et al.,2012).

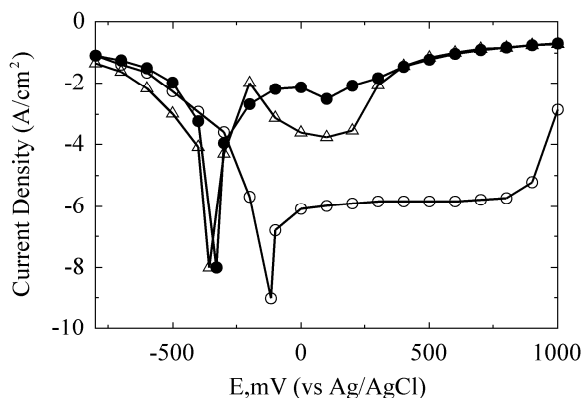


Fig. 3. Polarization curves of ● $\text{Ni}_3(\text{Si,Ti})$, △ type 304 and ○ C 276 in 0.5 kmol/ m^3 HCl solution at 303 K.

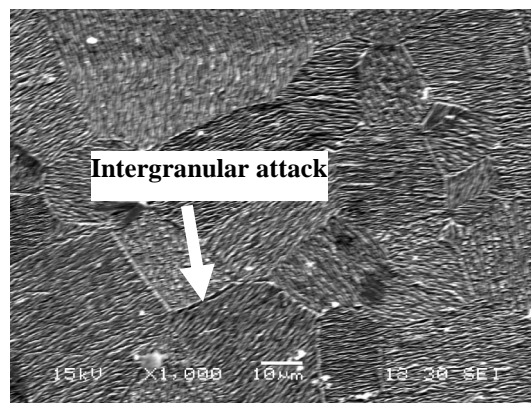


Fig. 4 Microstructure of $\text{Ni}_3(\text{Si,Ti})$ after immersion time 96 h in 0.5 kmol/ m^3 HCl solution at 303 K..

C. The corrosion property of $\text{Ni}_3(\text{Si,Ti})$

The presence of boron in homogenized $\text{Ni}_3(\text{Si,Ti})$ had the occurrence of the intergranular attack in acid solutions (Priyotomo et al.,2011; Priyotomo et al.,2012) as well as in the presence results. This would be related to the boron segregation at the grain boundaries (Takasugi et al.,1995). Furthermore, Priyotomo and co-workers had already investigated that the composition of the elements at the grain boundaries by the boron segregation would be different from that at grains; for instance, the amounts of Si and Ti at the grain boundaries would be smaller than those at the grains of homogenized $\text{Ni}_3(\text{Si,Ti})$ (Priyotomo et al.,2011). The difference in the composition between grains and grain boundaries could lead to the following things: (1) a potential difference between them and (2) a difference in film strength between on grains and grain boundaries, by which a degree of the film dissolution became different. Thus, it was concluded that the grain boundaries with the boron segregation would become the preferential sites for dissolution, causing the intergranular attack in $\text{Ni}_3(\text{Si,Ti})$ after thermomechanical process as well as that in homogenized $\text{Ni}_3(\text{Si,Ti})$ (Priyotomo et al.,2011 ; Priyotomo et al.,2012).

Furthermore, in the HCl solution which is very aggressive, it is known that the austenitic stainless steel such as type 304 has the highest weight loss as shown in Fig. 2. However, it was found that $\text{Ni}_3(\text{Si,Ti})$ had evidently the higher corrosion resistance than that of type 304, while type C 276 was the highest among them. This means that $\text{Ni}_3(\text{Si,Ti})$ was more resistant to chloride ion attack than type 304, while type C 276 had the highest resistance to that. From Fig 3, although a stable passive film cannot be formed in HCl solution for $\text{Ni}_3(\text{Si,Ti})$ and type 304 compared to C 276, a precipitated film was observed to be formed for both materials after the immersion test and was easily removed. The precipitated film would inhibit direct dissolution from metal surface and as a result influence a corrosion rate of the materials (Takasugi et al.,1995). Therefore, this implies that the precipitated film base on Ni, Si and Ti elements ($\text{Ni}_3(\text{Si,Ti})$) would inhibit the direct dissolution more efficiently than that on Fe, Cr and Ni elements (type 304), while the presence of Mo in C276 could restricted the susceptibility of corrosion attack by the presence of a stable passive film in chloride as well

as the results of Lillard and co-workers (Lillard et al.,1994).

IV. CONCLUSION

The corrosion behaviour of $\text{Ni}_3(\text{Si,Ti})$ after thermomechanical process in 0,5 kmol/m³ HCl solution has been studied and compared with that of type 304 and C276. The following summaries were obtained.

1. The intergranular attack was observed for $\text{Ni}_3(\text{Si,Ti})$ in HCl solution, which took place by boron segregation at grain boundaries.
2. $\text{Ni}_3(\text{Si,Ti})$ had the moderate corrosion resistance in HCl solution, while C276 and type 304 were the highest and the lowest corrosion resistances.
3. $\text{Ni}_3(\text{Si,Ti})$ was difficult to form a stable passive film as well as type 304, whereas C276 was easy to form that film.
4. A further experiment may be conducted to clarify the stability of film for $\text{Ni}_3(\text{Si,Ti})$ in detail.

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